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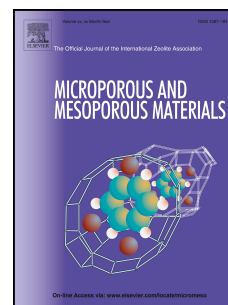
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Triptycene Structure-Directing Agents in Aluminophosphate Synthesis

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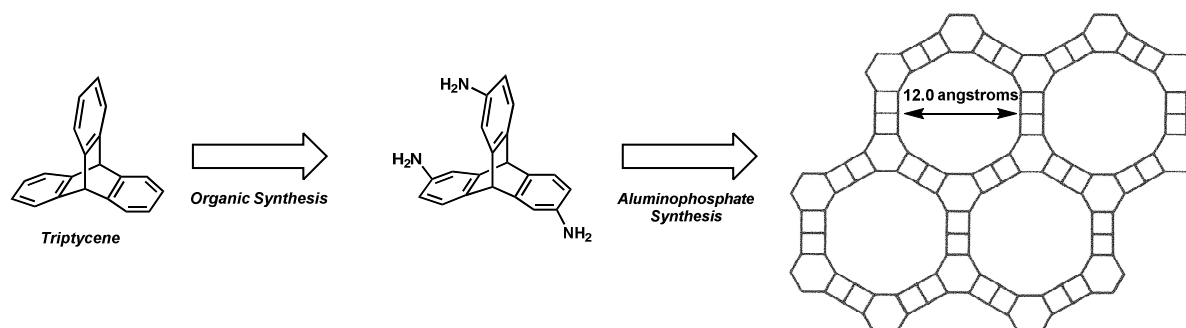
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ABSTRACT

The synthesis of aluminophosphates is investigated using a number of triptycene-based organic structure-directing agents (OSDA). These OSDAs are designed to synthesize extra-large pore and/or large cavity-containing molecular sieves. Starting from the hydrophobic triptycene molecule, OSDAs are prepared by introducing three amine-based centers that can be charged either by protonation in the acidic aluminophosphate reaction media or through quaternization. VPI-5 is synthesized using these triptycene OSDAs, and the OSDAs are occluded inside the pores. This synthesis marks the first time VPI-5 has been made as a single phase with an OSDA occluded inside the framework of the as-made material that is not removed by simple washing with water or other solvents. Additionally, several other aluminophosphates with unknown structures are synthesized using these new OSDAs.

GRAPHICAL ABSTRACT



1. Introduction

For both industrial and fundamental reasons, the synthesis of extra-large pore molecular sieves continues to be important [1, 2]. The lack of organic structure-directing agents (OSDA) with the appropriate properties to control the synthesis of these materials is just one of the issues that hinders the creation of extra-large pore materials. Organic molecules that are the appropriate size to fit within extra-large pore materials typically suffer from being too hydrophobic for the traditional molecular sieve synthesis (exceptions include those listed in refs 3 and 4). One solution to this problem is to introduce multiple charge centers into the OSDA. The creation of three charge centers in a single OSDA has seen limited use in the past to prepare molecular sieves [5, 6]. ZSM-18 was the first molecular sieve made with a triquaternized organic structure directing agent. ZSM-18 is a three dimensional zeolite with one 12 T-atom pore and has the rare zeolite feature of containing three T-atom rings [5]. While ZSM-18 does not contain extra-large pores, it does have a large cage where the OSDA resides. In addition to the aluminosilicate ZSM-18, ECR-40 is a silicoaluminophosphate with the equivalent topology [7]. More recently, our lab has used this concept of triquaternized structure directing agents in the synthesis of germanosilicate LTA [8].

Here, we report the synthesis of five OSDAs, all based on triptycene (Fig. 1), and their use in the synthesis of aluminophosphates. Triptycene is an intriguing SDA precursor because of its D_{3h} symmetry. SDA's with this space group have previously synthesized multi-dimensional large pore molecular sieves [9]. We hypothesized that the rigid ring system of triptycene would limit distortion of the OSDA in the molecular sieve synthesis. These OSDAs were used to make a known extra-large pore aluminophosphate (VPI-5), as well as three aluminophosphates products with unknown structure.

2. Experimental

2.1 Synthesis of organic structure-directing agents

Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of argon. All reagents were purchased from commercial sources and used as received. Compounds **1** and **5** were synthesized by adapting known procedures [10, 11]. Liquid NMR spectra were recorded on Varian Mercury spectrometers. High-resolution mass spectra were obtained from the California Institute of Technology mass spectrometry facility.

2,6,14-Triaminotriptycene 1. A 500 mL flask was charged with triptycene (7.50 grams, 29.50 mmols) and concentrated nitric acid (220 mL, 68.0-70.0 % by weight). The flask was fitted with a reflux condenser and heated to 80 °C for 2 hours. Reaction was cooled to 25 °C and poured into D. I. water (1300 mL). The resulting mixture was stirred for 10 minutes and then filtered and the resulting solids are collected. Solids were dissolved in CH_2Cl_2 (250 mL) and dry loaded onto silica gel (150 mL) using a rotary evaporator. The crude product was then purified by column chromatography on silica gel (eluent: 27% ethyl acetate: 73% Hexanes then 50% ethyl acetate: 50% Hexanes) to give 2,6,14-trinitrotriptycene (6.70 grams, 58-65% yield) as a yellow solid and 2,7,14-trinitrotriptycene (3.20 grams, 20-27% yield) as a yellow solid. 2,6,14-trinitrotriptycene. 1H NMR (500 MHz, $CDCl_3$): δ 8.34-8.32 (m, 3H), 8.07-8.03 (m, 3H), 7.66-7.62 (m, 3H), 5.83 (s, 1H), 5.82 (s, 1H). Spectral data match those previously reported [10, 11].

2,7,14-trinitrotriptycene. ^1H NMR (500 MHz, CDCl_3): δ 8.34 (d, J = 2.2 Hz, 3H), 8.05 (dd, J = 8.2, 2.2 Hz, 3H), 7.62 (d, J = 8.2 Hz, 3H), 5.84 (s, 1H), 5.80 (s, 1H). Spectral data match those previously reported [10, 11]. A 1 L flask was charged with 2,6,14-trinitrotriptycene (6.70 grams, 17.21 mmols), THF (80 mL), and Raney nickel (1.00 grams). The flask was fitted with a reflux condenser and the solution was heated to 65 °C. Hydrazine mono hydrate was added in 1 mL portions (16.00 mL, 206.51 mmols), after addition of hydrazine vigorous bubbling was observed, the next aliquot of hydrazine was added after bubbling subsided. After all of the hydrazine was consumed, the reaction was cooled to room temperature and filtered over a small pad of celite. The flask and pad were washed with ethanol (3 x 30 mL). The filtrate was evaporated under reduced pressure to afford 2,6,14-triaminotriptycene **1** (4.37 g, 85 % yield) as a brown solid and was used without further purification. ^1H NMR (400 MHz, CDCl_3): δ 7.07-7.04 (m, 3H), 6.73-6.69 (m, 3H), 6.26-6.21 (m, 3H), 5.04 (s, 1H), 5.02 (s, 1H), 3.46 (s, 6H). Spectral data match those previously reported [10, 11]. 2,6,14-triaminotriptycene **1** can decompose over time if left standing at room temperature for several weeks. 2,6,14-triaminotriptycene **1** was purified by column chromatography periodically (solvent system; 75% CH_2Cl_2 :24%EtOAc:1%Et₃N).

2,7,14-Triaminotriptycene **5**. 2,7,14-triaminotriptycene was synthesized identically to 2,6,14-triaminotriptycene **1** from 2,7,14-trinitrotriptycene. 2,7,14-triaminotriptycene **5** (2.09 g, 85 % yield) was obtained as a brown solid and was used without further purification. ^1H NMR (400 MHz, CDCl_3): δ 7.05 (d, 3H), 6.74 (d, 3H), 6.25 (dd, 3H), 5.07 (s, 1H), 5.00 (s, 1H), 3.49 (s, 6H). Spectral data match those previously reported [10, 11].

2,6,14-N-methyltriaminotriptycene **2**. A 250 mL flask is charged with 2,6,14-triaminotriptycene **1** (3.00 grams, 10.02 mmol), THF (100 mL, dried over molecular sieves), and anhydrous pyridine (16 mL). Reaction was cooled to 0 °C and ethyl chloroformate (7.20 mL, 75.16 mmols). Reaction was allowed to gradually warm to 25 °C and stirred for an additional hour. The reaction mixture was evaporated under reduced pressure and dry loaded onto silica gel. The crude product was purified by column

chromatography on silica gel (eluent: 25% ethyl acetate: 75% hexanes → 40% ethyl acetate: 60% hexanes → 60% ethyl acetate: 40% hexanes) to give 2,6,14-N-ethylcarbamoyltriaminotriptycene (4.20 grams, 81% yield) as an orange solid. ^1H NMR (300 MHz, CDCl_3): δ 7.60-7.52 (m, 3H), 7.27-7.22 (m, 3H), 6.87-6.79 (m, 3H), 6.46 (s, 3H), 5.07-5.05 (m, 2H), 4.18 (q, J = 6 Hz, 6H) 1.28 (t, J = 6 Hz, 9H). A 250 mL flask fitted with a reflux condenser was charged with 2,6,14-N-ethylcarbamoyltriaminotriptycene (4.20 grams, 8.10 mmols) and THF (60 mL). This reaction was cooled to 0 °C. Lithium aluminum hydride (3.00 grams, 80.02 mmols) was added, and the reaction was stirred for 1 hour at 0 °C. The reaction was warmed to 25 °C and stirred for 5 minutes. The reaction was then refluxed at 95 °C for 3 hours. The reaction was cooled back down to 0 °C and celite (50 mL) was added. D. I. water was slowly added in portions until all unreacted lithium aluminum hydride was quenched. Reaction slurry was filtered and washed with ethyl acetate (3 x 40 mL). The filtrate was dry loaded onto silica gel under reduced pressure and purified by column chromatography on silica gel (eluent: 39% ethyl acetate: 60% hexanes: 1% triethyl amine → 69 % ethyl acetate: 30% hexanes: 1% triethyl amine) to give 2,6,14-N-methyltriaminotriptycene **2** (2.07 grams, 75% yield) as an orange solid. ^1H NMR (300 MHz, CDCl_3): δ 7.14-7.09 (m, 3H), 6.71-6.69 (m, 3H), 6.21-6.16 (m, 3H), 5.07-5.05 (m, 2H), 2.82-2.71 (m, 12H). ^{13}C NMR (125 MHz, CDCl_3): δ 147.7, 147.0, 146.2, 145.9, 1, 134.2, 123.5, 123.2, 109.5, 109.2, 108.7, 108.5, 54.24, 52.6, 41.3. HRMS-ESI (m/z) [$\text{M}]^+$ calcd for $\text{C}_{23}\text{H}_{23}\text{N}_3$, 341.1892; found 341.1886.

2,6,14-N,N-dimethyltriaminotriptycene **3**. A 250 mL flask was charged with 2,6,14-triaminotriptycene **1** (1.24 grams, 4.14 mmols), paraformaldehyde (0.87 grams, 29.05 mmols), and acetic acid (20 mL). To this reaction mixture was added sodium cyanoborohydride (1.83 grams, 29.05) in three portions. The reaction was then stirred for 4 hours at 25 °C. The reaction was then slowly neutralized with NaOH aqueous solution (100 mL, 20% by weight). Reaction is then filtered and orange solid is collected. The solids were dissolved in CH_2Cl_2 (50 mL) and dry loaded onto silica gel under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: 30%

diethyl ether, 69% hexanes, 1% triethyl amine) to give 2,6,14-N,N-dimethyltriaminotriptycene **3** (0.88 grams, 55% yield) as a light orange solid. ^1H NMR (500 MHz, CDCl_3): δ 7.19 (d, J = 10 Hz, 1H), 7.16 (d, J = 10 Hz, 2H), 6.87 (d, J = 5 Hz, 2H), 6.84 (d, J = 5 Hz, 1H), 6.30-6.27 (m, 3H), 5.13 (s, 1H), 5.12 (s, 1H), 2.85 (s, 18 H). ^{13}C NMR (125 MHz, CDCl_3): δ 148.8, 148.6, 147.6, 147.0, 136.2, 135.2, 123.8, 123.5, 109.7, 109.4, 108.7, 108.3, 53.8, 52.6, 31.7. HRMS-ESI (m/z) [M] $^{+}$ calcd for $\text{C}_{26}\text{H}_{29}\text{N}_3$, 383.2361; found 383.2347.

2,6,14-N,N,N-trimethyltriammoniumtriptycene tribromide **4**. A 100 mL flask was charged with 2,6,14-triaminotriptycene **1** (2.57 grams, 8.60 mmols) and dimethylformamide (11 mL). This solution was cooled to 0 °C. N,N-diethyl aniline (8.2 mL, 51.6 mmols) was added, followed by the addition of methyl iodide (9.80 mL, 157.4 mmols) in a drop wise fashion. The reaction was slowly warmed to 25 °C and stirred for an additional 24 hours. Solids are filtered and recrystallized from absolute ethanol to give 2,6,14-N,N,N-trimethyltriammoniumtriptycene triiodide (5.57 grams, 80% yield) as a light pink solid. ^1H NMR (400 MHz, D_2O): δ 8.11 (d, J = 4 Hz, 2H), 8.08 (d, J = 4 Hz, 1H), 7.81-7.78 (m, 3H), 7.60-7.57 (m, 3H), 6.09 (m, 2H), 3.61 (s, 27H). A Teflon jar was charged with 2,6,14-N,N,N-trimethyltriammoniumtriptycene triiodide (4.00 grams, 5.06 mmols) methanol (40 mL) and water (10 mL). Bromide exchange resin [12] (46 mL) was added and the reaction mixture was stirred at 25 °C for 12 hours. Reaction is filtered and washed with methanol (5 x 50 mL). The filtrate was evaporated under reduced pressure and resulting solid is recrystallized from absolute ethanol to give 2,6,14-N,N,N-trimethyltriammoniumtriptycene tribromide **4** (1.68 grams, 50% yield) as a pale orange solid. ^1H NMR (400 MHz, D_2O): δ 8.08-8.06 (m, 3H), 7.79-7.76 (m, 3H), 7.59-7.56 (m, 3H), 6.07 (s, 1H), 6.05 (s, 1H), 3.60 (s, 27H). ^{13}C NMR (125 MHz, D_2O): δ 146.1, 146.0, 145.8, 145.7, 144.3, 144.2, 125.6, 125.5, 117.4, 117.3, 116.2, 116.1, 57.0, 52.3, 51.7. HRMS-ESI (m/z) [M] $^{+}$ calcd for $\text{C}_{29}\text{H}_{38}\text{N}_3 \text{Br}_2$, 588.1412; found (588.1412).

2.2 Synthesis of AlPO_4 molecular sieves

All reactions were performed in 23 mL Teflon-lined stainless steel autoclaves (Parr instruments). Reactions were tumbled at approximately 40 rpm using spits built into convection ovens. Phosphorus

source was ortho-phosphoric acid (85.0% H_3PO_4 , Fisher scientific). Aluminum source was pseudoboehmite (74.5% Al_2O_3 , Sasol).

Gels for AlPO_4 reactions were prepared by adding phosphoric acid to a mixture of pseudoboehmite and distilled, de-ionized H_2O (DDI H_2O). This mixture is stirred at 25 °C for 3 hours. OSDA was then added and stirred for an additional 2 hours. The autoclave was then capped and put into either the 140 or 160 °C oven. The reactors were opened every 24-48 h to assess reaction progress. After homogenizing, a small sample was successfully washed with D.I. H_2O (2 x 10 mL) and acetone: methanol (1:1, 3 x 10 mL) and the XRD pattern was inspected. All reactions were monitored for at least 1 week. Synthesis of AlPO-H3 was reproduced from a previously reported procedure [13].

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were collected using a Rigaku Miniflex II diffractometer and Cu K α -radiation. ^{13}C solid-state magic angle spinning nuclear magnetic (CP-MAS NMR) spectra were recorded on either a Bruker Avance 500 MHz spectrometer with a Bruker 4mm MAS probe or a Bruker Avance 200 MHz spectrometer with a Bruker 7 mm MAS probe. ^{27}Al and ^{31}P solid-state magic angle spinning nuclear magnetic (MAS NMR) spectra were recorded on a Bruker AM 300 spectrometer. Aluminophosphate samples were packed into either 7 or 4 mm ZrO_2 rotors with Kel-F caps and spun at 4, 8, or 14 kHz. ^{13}C , ^{27}Al , and ^{31}P NMR spectra were recorded at operating frequencies of 75, 75, and 120 MHz respectively. ^{27}Al NMR chemical shifts are referenced to a 1.0 M $\text{Al}(\text{NO}_3)_3$ solution (0.00 ppm) and are not corrected for second order quadrupolar effects. ^{13}C NMR spectra were measured using cross-polarization with a ^1H -90° pulse. ^{13}C NMR chemical shifts are referenced to adamantane (downfield resonance at 38.4 relative to tetramethylsilane). ^{31}P NMR chemical shifts are referenced to an 85% H_3PO_4 solution (0.00 ppm). Simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed using a Netzsch STA 449 C instrument. Samples (0.01-0.06 g) were

placed in aluminum crucible and heated at 1 K/min in a flowing stream ($0.667 \text{ cm}^3/\text{s}$) comprised of 50% air (Air Liquide, breathing grade) and 50% argon (Air Liquide, UHP).

3. Results and Discussion

3.1 Overview of aluminophosphate syntheses

Results of the aluminophosphate screening reactions are presented in Tables 1 and 2. Typical synthesis compositions are: $1.0 \text{ P}_2\text{O}_5$: $1.0 \text{ Al}_2\text{O}_3$: 0.65 SDA : $X \text{ H}_2\text{O}$ @ 140 or $160 \text{ }^\circ\text{C}$, where X is either 40 or 80 . VPI-5 was synthesized under a number of conditions with several different OSDAs, but the stability of this product in the synthesis mixture at reaction temperature varied. VPI-5 was most stable at the lower temperature and in more dilute synthesis mixtures. 2,6,14-triaminotriptycene **1** produced VPI-5 under almost all conditions screened. In addition to VPI-5, three unknown phases were synthesized.

3.2. 2,6,14-triaminotriptycene **1** and the synthesis of VPI-5

The extra-large pore aluminophosphate VPI-5 [14, 15] is formed in the presence of 2,6,14-triaminotriptycene **1** at a synthesis composition of: $1.0 \text{ P}_2\text{O}_5$: $1.0 \text{ Al}_2\text{O}_3$: 0.65 2,6,14-triaminotriptycene: $80 \text{ H}_2\text{O}$ @ $140 \text{ }^\circ\text{C}$. The XRD pattern of this product can be seen in Fig. 2[15]. To our surprise, the VPI-5 product was very stable in the synthesis medium at the synthesis conditions, and was observed after 1 week at $140 \text{ }^\circ\text{C}$ with no other byproducts present (unlike other syntheses of VPI-5 that lead to its degradation in the synthesis mixture).

Thermogravimetric analysis and solid-state ^{13}C MAS NMR were performed on the sample of VPI-5 to observe whether or not the organic was occluded and intact. Thermogravimetric analysis of the as-made VPI-5 showed an endothermic mass loss below $200 \text{ }^\circ\text{C}$ of 13.3% that is attributed to the loss of occluded water and an exothermic mass loss above $260 \text{ }^\circ\text{C}$ of 9.9% that is attributed to occluded organic material. From these TGA data and previous reports of the void space of VPI-5 [15], it appears that all of the organic loss and a majority ($\sim 87\%$) of the water loss could be from OSDA and

water, respectively, residing in the pores of VPI-5. The OSDA must reside in the one-dimensional extra-large pores and there is sufficient volume in VPI-5 to accommodate the amount of the organic measured by TGA. In previous syntheses of VPI-5 with an OSDA, the structure directing agent was not tightly held within the framework and was not observed in the as-made material after collection and washing. Comparing the ^{13}C MAS NMR of the VPI-5 sample to the OSDA alone (Fig. 3) indicates that the organic is intact inside the aluminophosphate. The peak broadening of the ^{13}C resonances in the VPI-5 spectra indicate a lack of OSDA mobility, and suggest that it is tightly held within the pore system of the framework [16]. The ^{13}C NMR data alone are not sufficient to determine whether or not all or a portion of the amine residing in the VPI-5 are protonated.

^{27}Al and ^{31}P MAS NMR (Figs. 4 and 5) of the VPI-5 with the organic occluded matched closely to the reported data for this material [17]. ^{27}Al MAS NMR has two peaks, one for aluminum in a tetrahedral coordination environment (~ 40 ppm) and one for an octahedral coordination environment (~ 28 ppm). ^{31}P MAS NMR shows 3 distinct chemical environments that is reported for highly crystalline VPI-5 [17]. Additionally, a small broad peak is observed at -16.6 ppm, and this resonance is likely from $\text{P}-\text{O}^-$ groups (in an amount well below the amount of the occluded organic). The area of this peak is about 13% of the total phosphorus spectrum. A similar peak, although of much smaller area, is observed in the synthesis of VPI-5 that does not contain occluded organic [18].

This synthesis marks the first time VPI-5 has been made as a single phase with an OSDA occluded inside the framework of the as-made material that is not removed by simple washing with water or other solvents. The presence of the OSDA within the pores of the VPI-5 maybe a reason why it is so stable in the synthesis mixture.

3.3. Altering the basicity and polarity of 2,6,14-triaminotriptycene **1** and the synthesis of unknown aluminophosphates

OSDAs **2**, **3** and **4** were prepared (Fig. 1), and used as OSDAs in aluminophosphate syntheses. Aluminophosphate syntheses using the triquaternized SDA **4** resulted in only amorphous material at all of the reported temperatures and H₂O ratios reported after one week. Aluminophosphate syntheses using SDAs **2** and **3** resulted in what appears to be an unknown aluminophosphate products. XRDs of these unknown aluminophosphate products show a striking similarity to AlPO₄-H₃ (Figs. 7 and 8) [19, 21].

The OSDAs used here are drastically larger than the void space of AlPO₄-H₃ [20], so the samples were investigated further to observe whether or not the OSDA remains intact. Thermogravimetric analysis of the aluminophosphate product with dimethyl SDA **3** gave an endothermic mass loss of 11% below 200 °C (associated with water loss) and an exothermic mass loss of 8.3% after 260 °C (associated with organic loss). Thermogravimetric analysis of the aluminophosphate product with mono-methyl SDA **2** gave an endothermic mass loss of 10.3% below 200 °C and an exothermic mass loss of 6.5% after 260 °C. These weight losses are slightly smaller but similar to what is observed for VPI-5. Unfortunately both of these unknowns are unstable to calcination and ozonolysis, and sonication of the samples does not remove significant amounts of the occluded organic. For these reasons, adsorption pore volumes cannot be obtained. ¹³C NMR spectroscopy of the unknown aluminophosphate products are shown in Figs. 9 and 10. The ¹³C MAS NMR spectra of these phases is difficult to conclusively interpret. It appears that the N-CH₃ peaks have shifted downfield from ~35 ppm to ~55 ppm. This shift could be from protonation of the nitrogen atoms. The sharpness of the methyl peak in Fig. 10 is interesting and attributed to the monomethyl SDA **2** not fitting tightly into the inorganic framework and thus allowing for bond rotation [16].

The ¹³C NMR data suggest that the OSDAs may be intact for these two unknown phases. If this is the case, then they cannot be AlPO₄-H₃. The ²⁷Al MAS NMR spectrum of the aluminophosphate phase with mono-methyl SDA **2** has two resonances, one resonance corresponding to aluminum in a

tetrahedral coordination environment (40.6 ppm) and a broad resonance corresponding to aluminum in an octahedral coordination environment (-12.5 - -39.0 ppm) (Fig. 11). Although the ^{27}Al NMR spectrum seems to match reasonably well with $\text{AlPO}_4\text{-H3}$ (Fig. 13), the proportion of octahedral aluminum in our sample is much smaller than that of the reported $\text{AlPO}_4\text{-H3}$ spectra. The ^{31}P NMR spectrum (Fig. 12) has two resonances (-24.2 and -26.6 ppm). In our as-made sample of $\text{AlPO}_4\text{-H3}$ these signals are in close to a 1 to 1 ratio and a third peak is observed at -29.4 ppm (Fig.14), in the case of the unknown it appears that the signal at -26.6 ppm is at least twice the size of the peak at -24.2 ppm. In $\text{AlPO}_4\text{-H3}$ the 2 phosphorus signals are differentiated by their outer coordination environment, the phosphorus atoms at ~ 24 ppm are connected to more octahedrally coordinated aluminum atoms, while the phosphorus atoms at ~ 26 ppm are attached to more tetrahedrally coordinated aluminum atoms [20]. In the unknown, there is less octahedral aluminum than in $\text{AlPO}_4\text{-H3}$ and a larger proportion of the phosphorus at -26 ppm. We do not observe a signal for P-O^- in this unknown. Further work is required to fully identify this unknown phase.

The ^{27}Al and ^{31}P MAS NMR spectra of the unknown aluminophosphate phase occluded with 2,6,14-N,N-dimethyltriaminotriptycene **3** (Figs. 15 and 16) make it clear that this product is not $\text{AlPO}_4\text{-H3}$. The ^{27}Al MAS NMR matches closely to what is reported for $\text{AlPO}_4\text{-H3}$ (Fig. 13), it is comprised of 2 regions, the first is a narrow resonance at 40.6 ppm corresponding to 4-coordinated aluminum and the second is broad resonance centered around -25 ppm that is characteristic of aluminum in an octahedral environment. The ^{31}P MAS NMR spectrum is very different from what is reported for $\text{AlPO}_4\text{-H3}$. The ^{31}P MAS NMR spectrum of $\text{AlPO}_4\text{-H3}$ consists of 3 peaks at -24, -25.6 and -29 ppm (Fig. 14). The peak at -24 ppm is associated with phosphorus atoms in the 6^3 sheet and is bonded to more octahedral aluminum atoms. The peak at -26 ppm is associated with phosphorus atoms in the 4.8^2 sheet and is bonded to more tetrahedral aluminum atom [20]. The ^{31}P MAS NMR spectrum of this unknown consist of 3 peaks

at -21.4, -25.4, and -31.5 ppm. This spectrum is more like the ^{31}P MAS NMR of the double four-rings observed in structures such as VPI-5 and AlPO-H2 [17, 22].

3.4. Aluminophosphate synthesis using the structural isomer 2,7,14-triaminotriptycene **5**

We explored the use of the closely related structural isomer 2,7,14-triaminotriptycene **5** in the synthesis of aluminophosphates (Table 1). Not surprisingly, when this SDA was used with a synthesis composition of: 1.0 P_2O_5 : 1.0 Al_2O_3 : 0.65 2,7,14-triaminotriptycene: 80 H_2O @ 140 °C, VPI-5 is observed by XRD. However, when this synthesis composition was altered to: 1.0 P_2O_5 : 1.0 Al_2O_3 : 0.65 2,7,14-triaminotriptycene: 40.0 H_2O @ 160 °C, we observed by XRD an unknown phase with a low angle peak that corresponds to a large d-spacing (18.7 angstroms) (Fig. 17). When the synthesis composition was changed to: 1.0 P_2O_5 : 1.0 Al_2O_3 : 0.65 2,7,14-triaminotriptycene: 40.0 H_2O @ 140 °C, we observed an initial mixture of VPI-5 and this new unknown phase, that slowly over time, completely transformed to this new unknown phase (Fig. 18). This new unknown phase was stable to copious washings at room temperature with a variety of solvents and for extended drying periods at 100 °C (10-14 hours). Unfortunately, it was unstable to calcination to 540 °C in air and washings at 100 °C with dimethylformamide, ethanol, or methanol.

Thermogravimetric analysis and ^{13}C CP MAS NMR of this new unknown phase is consistent with a layered aluminophosphate phase. In the thermogravimetric analysis of the as-made, unknown phase there was an exothermic mass loss of 38.9 % after 180 °C, consistent with large amounts of occluded organic within a layered material. The ^{13}C CP MAS NMR spectrum of this material shows that the OSDA is intact post synthesis (Fig. 19). The resonances from this aluminophosphate are much sharper than what is observed for any of the other AlPO_4 products suggesting that the SDA is organizing within this

inorganic structure differently. The peak sharpening of the ^{13}C resonances in Figure 19 indicate an increase in OSDA mobility [16].

^{27}Al and ^{31}P MAS NMR spectra of this new phase are illustrated in Figs. 20 and 21, respectively. The ^{27}Al NMR spectrum shows that the aluminum is primarily in a tetrahedral coordination environment (35.9 ppm) with a very small amount octahedrally coordinated (~ -10 ppm). The ^{31}P NMR spectrum of this phase shows 3 main resonances of close to equal intensity (-23.0, -25.4, -26.6) as well as two minor peaks in the P-O $^-$ region (-10.6, -17.0), that might be balancing protonated organic SDAs.

4. Conclusions

The structure-directing effects of triptycene derivatives containing three amines provided a new way to synthesize VPI-5. The VPI-5 synthesis yielded a product that for the first time has OSDA occluded inside its pores that was not removed via washings with water and other solvents. The occluded organic made the VPI-5 product extremely stable to the synthesis conditions. Subtle changes in the structure of the triptycene-based OSDA lead to the synthesis of several unknown products.

5. Acknowledgements

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7. Tables

Table 1: Phases obtained from aluminophosphate reactions @ 140 °C

SDA	H ₂ O/P ₂ O ₅ =40 (Time)	H ₂ O/ P ₂ O ₅ =80 (Time)
2,6,14-triaminotriptycene 1	VPI-5 (2 days)	VPI-5 (2 days)
2,6,14-N-methyltriaminotriptycene 2	Unknown i (2 days)	VPI-5 (2 days)
2,6,14-N,N-dimethyltriaminotriptycene 3	Unknown ii (2 days)	Dense phases
2,6,14-N,N,N-trimethyltriammoniumtriptycene tribromide 4	Amorphous	Amorphous
2,7,14-Triaminotriptycene 5	Unknown iii	VPI-5 (2 days)

Table 2: Phases obtained from aluminophosphate reactions @ 160 °C

SDA	H ₂ O/ P ₂ O ₅ =40 (Time)	H ₂ O/ P ₂ O ₅ =80 (Time)
2,6,14-triaminotriptycene 1	Dense phases	VPI-5 (1 days)
2,6,14-N-methyltriaminotriptycene 2	Unknown i (2 days)	Dense phases (2 days)
2,6,14-N,N-dimethyltriaminotriptycene 3	Dense phases (2 days)	Dense phases
2,6,14-N,N,N-trimethyltriammoniumtriptycene tribromide 4	Amorphous	Amorphous
2,7,14-Triaminotriptycene 5	Unknown iii	Dense phases (2 days)

8. Figure titles

Figure 1: Triptycene structure directing agents investigated

Figure 2: XRD pattern for as-made VPI-5 with SDA 1

Figure 3: VPI-5 and SDA 1

Figure 4: ^{13}C CP MAS NMR of: as-made VPI-5 (top) and SDA 1 (bottom), * denote spinning side bands

Figure 5: ^{27}Al MAS NMR of as-made VPI-5

Figure 6: ^{31}P MAS NMR of as-made VPI-5

Figure 7: XRD patterns of unknown AlPO_4 s and AlPO_4H_3 : with dimethyl SDA 3 (top), monomethyl SDA 2 (middle), and $\text{AlPO}_4\text{-H}_3$ (bottom)

Figure 8: $\text{AlPO}_4\text{-H}_3$ and SDA 2

Figure 9: ^{13}C CP MAS NMR of: as-made aluminophosphate unknown ii (top) and SDA 3 (bottom), * denote spinning side bands

Figure 10: ^{13}C CP MAS NMR of: as-made aluminophosphate unknown i (top) and SDA 2 (bottom), * denote spinning side bands

Figure 11: ^{27}Al MAS NMR of unknown AlPO_4 with SDA 2

Figure 12: ^{31}P MAS NMR of unknown AlPO_4 with SDA 2

Figure 13: ^{27}Al MAS NMR of as-made $\text{AlPO}_4\text{-H}_3$

Figure 14: ^{31}P MAS NMR of as-made $\text{AlPO}_4\text{-H}_3$

Figure 15: ^{27}Al MAS NMR of unknown AlPO_4 with SDA 3

Figure 16: ^{31}P MAS NMR of unknown AlPO_4 with SDA 3

Figure 17: XRD pattern for as-made unknown aluminophosphate with SDA 5

Figure 18: XRD patterns of aluminophosphate synthesis over time with SDA 5 @ 140 °C

Figure 19: ^{13}C CP MAS NMR of: as-made aluminophosphate unknown iii (top) and SDA 5 (bottom), * denote spinning side bands

Figure 20: ^{27}Al MAS NMR of unknown aluminophosphate with SDA 5

Figure 21: ^{31}P MAS NMR of unknown aluminophosphate with SDA 5

9. Figures

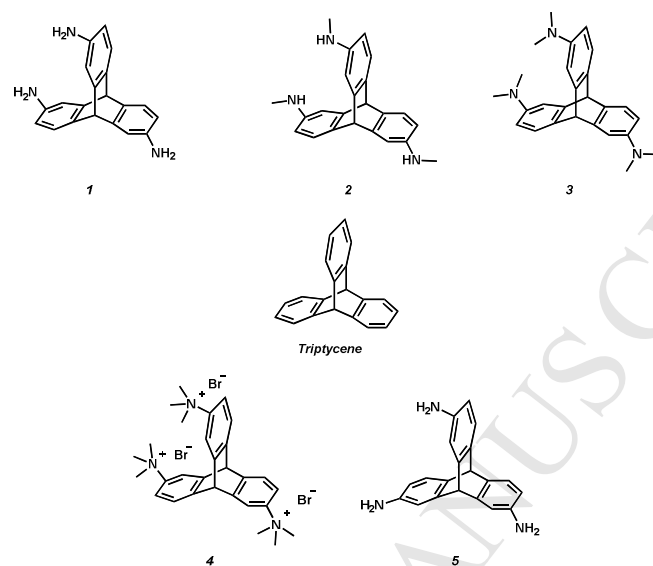


Figure 1

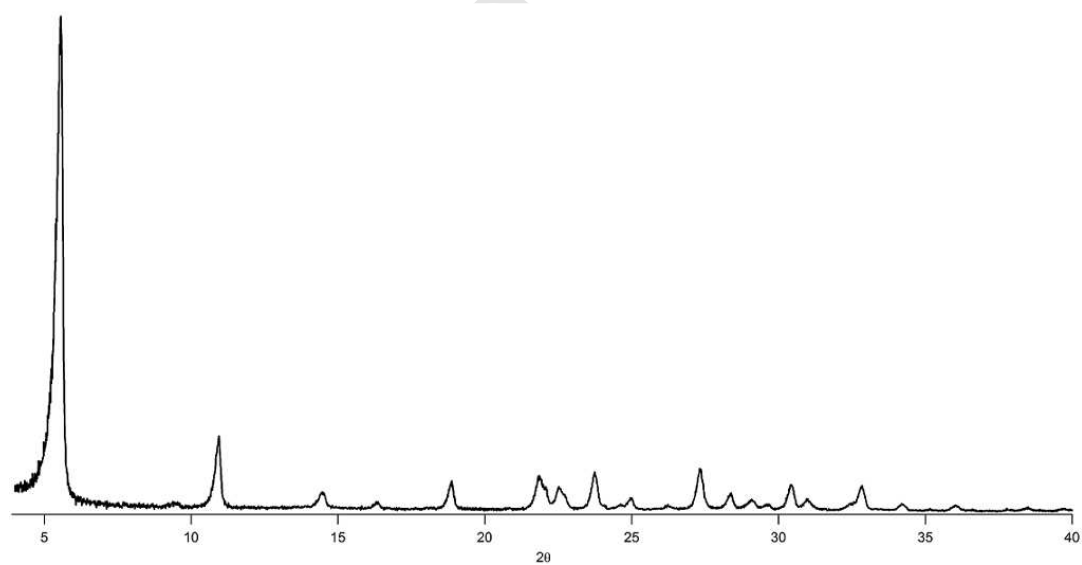


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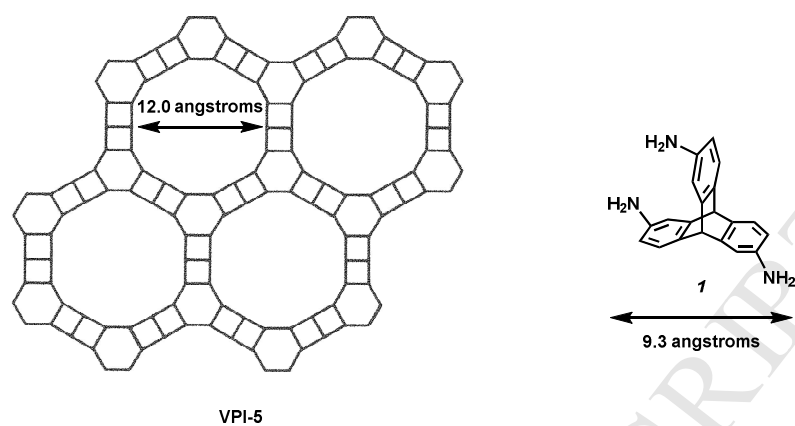


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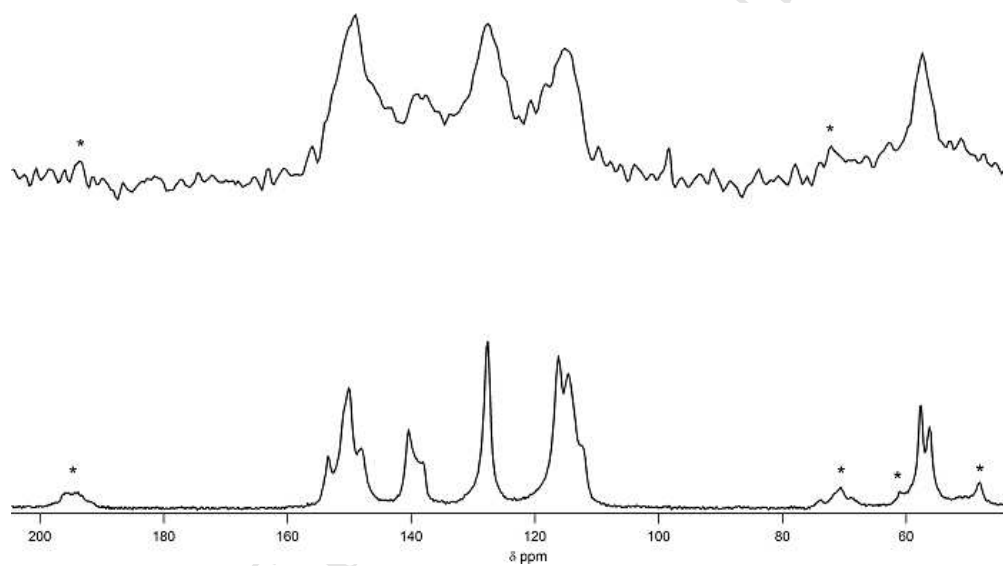


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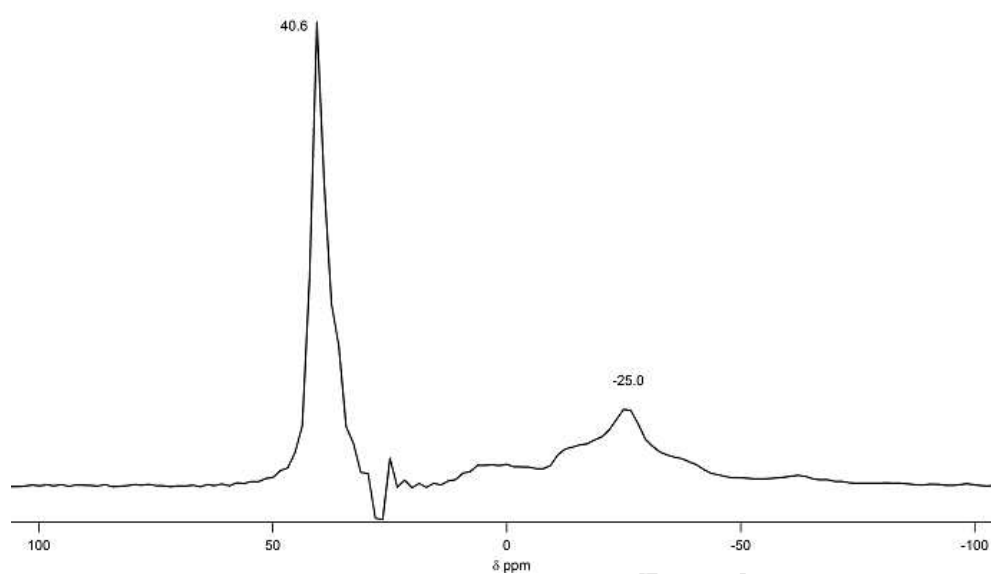


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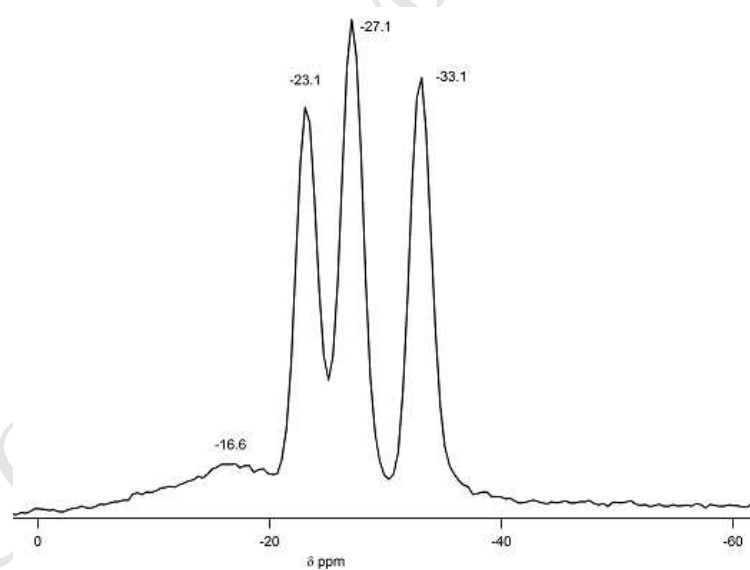


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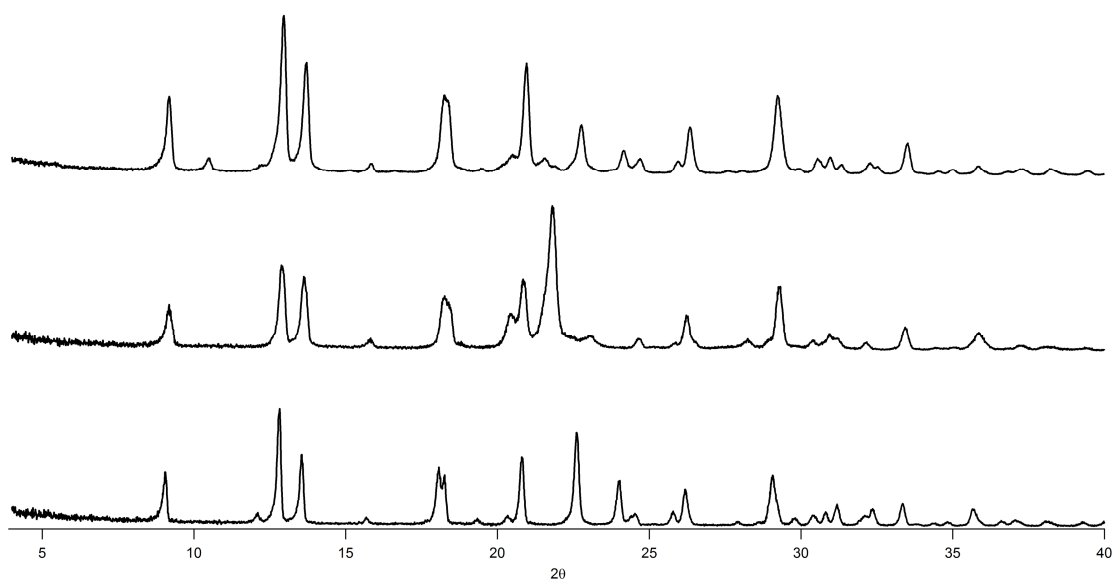


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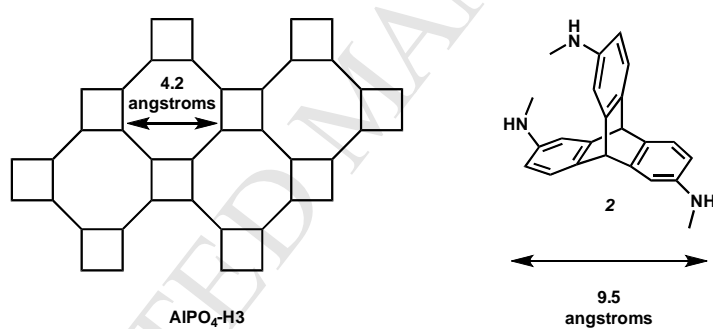


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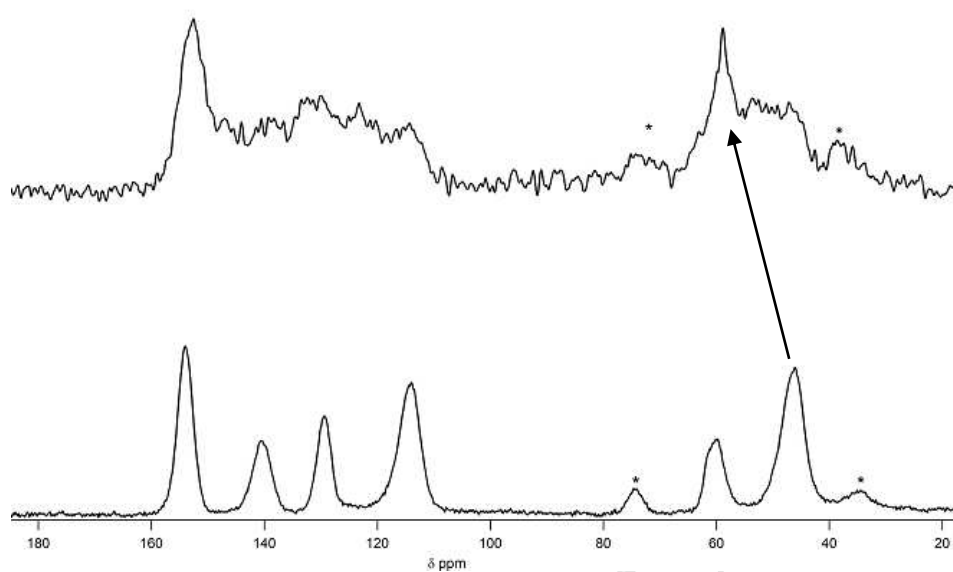


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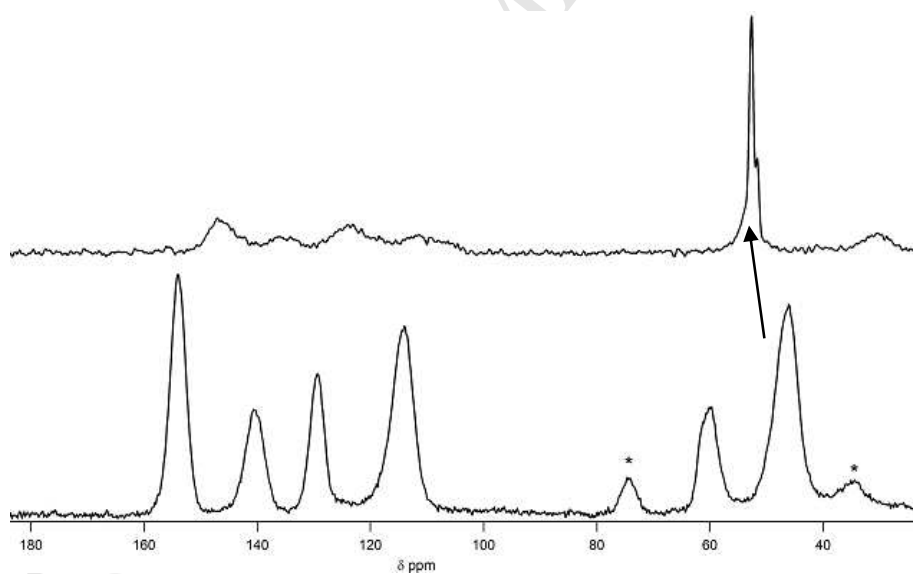
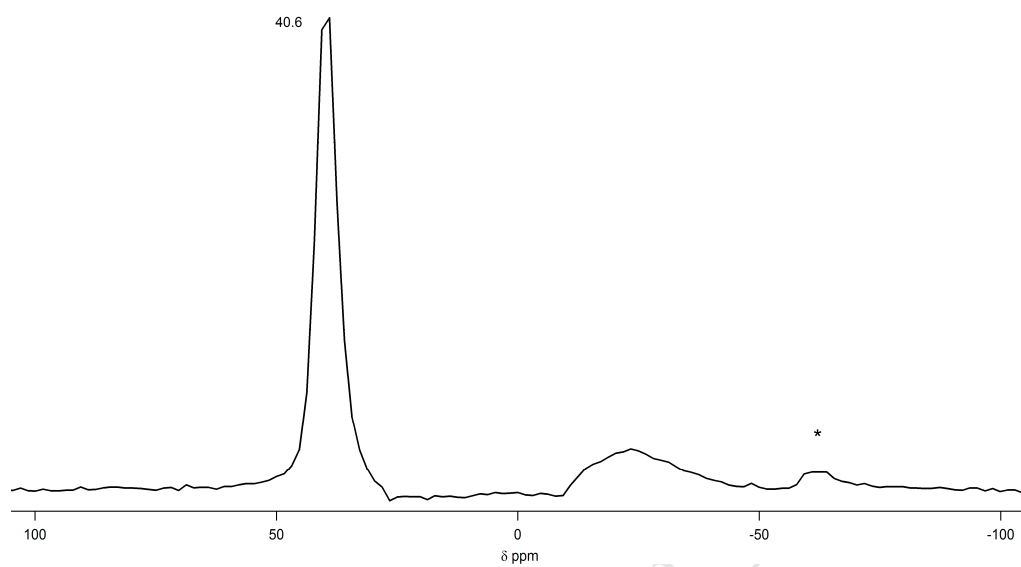
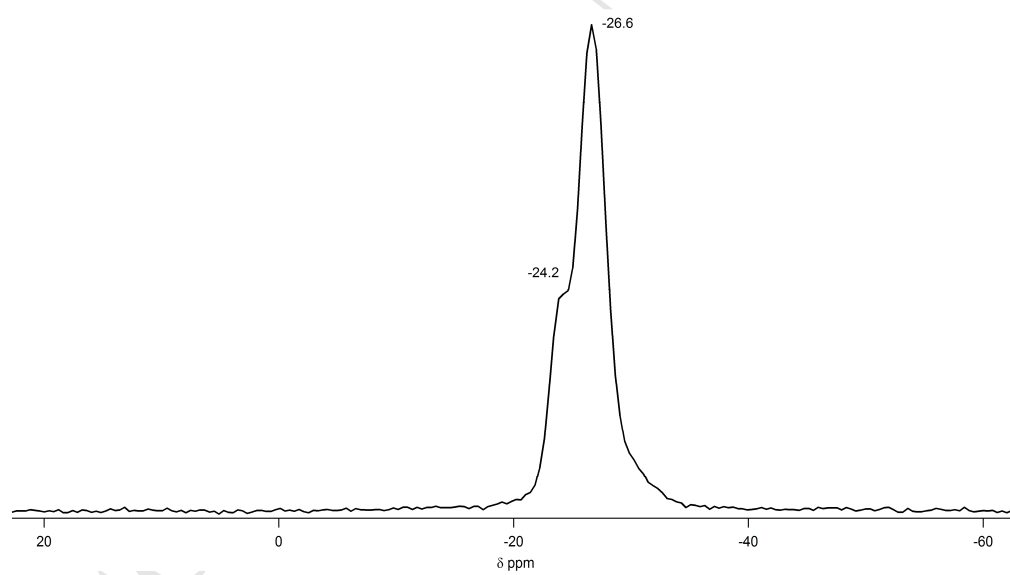
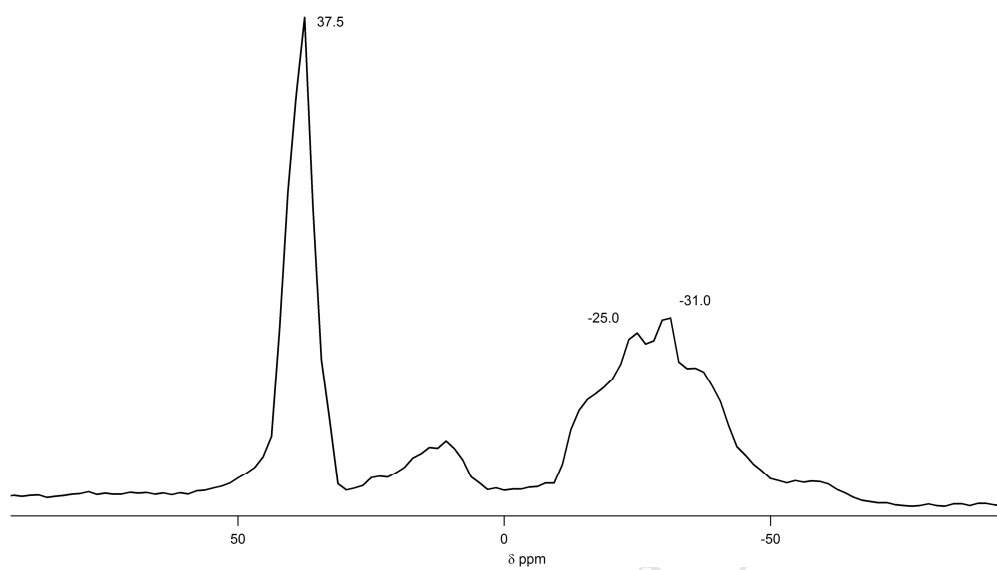
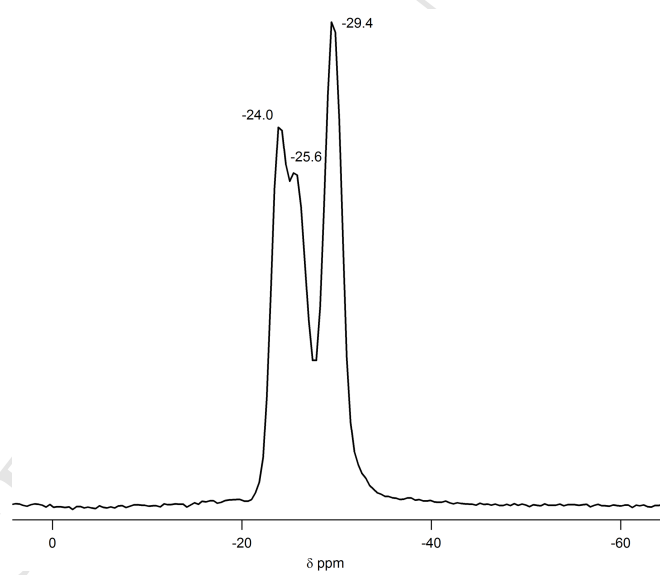
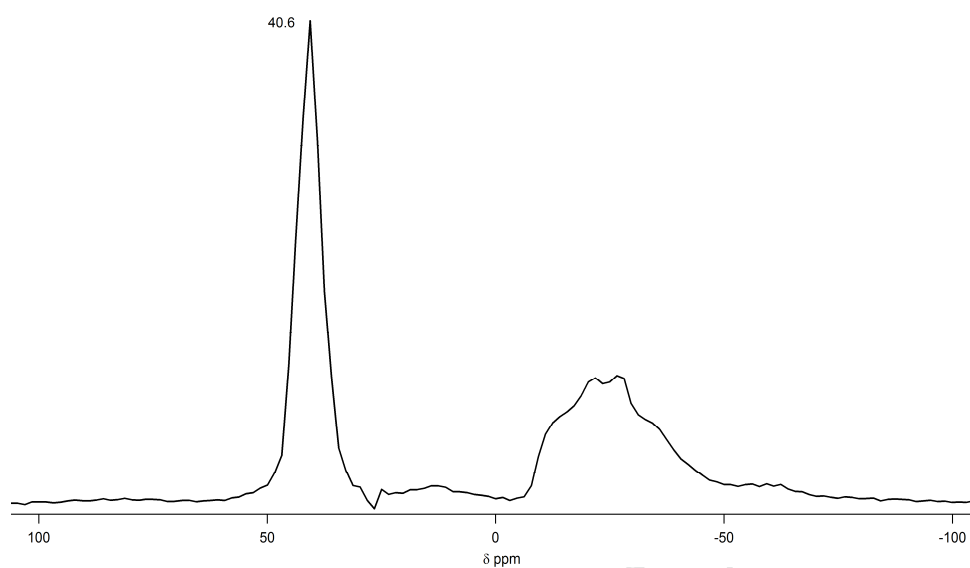
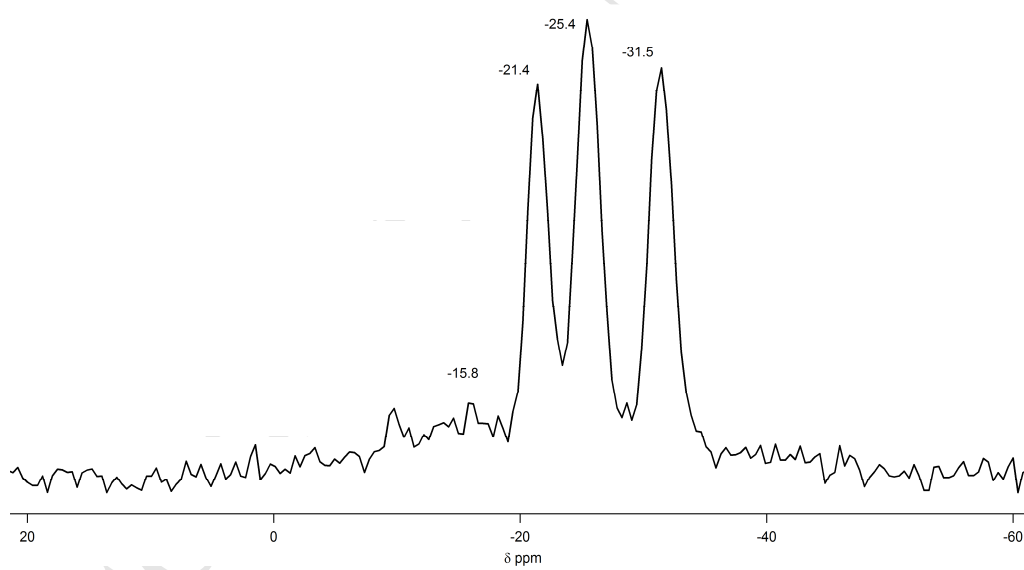
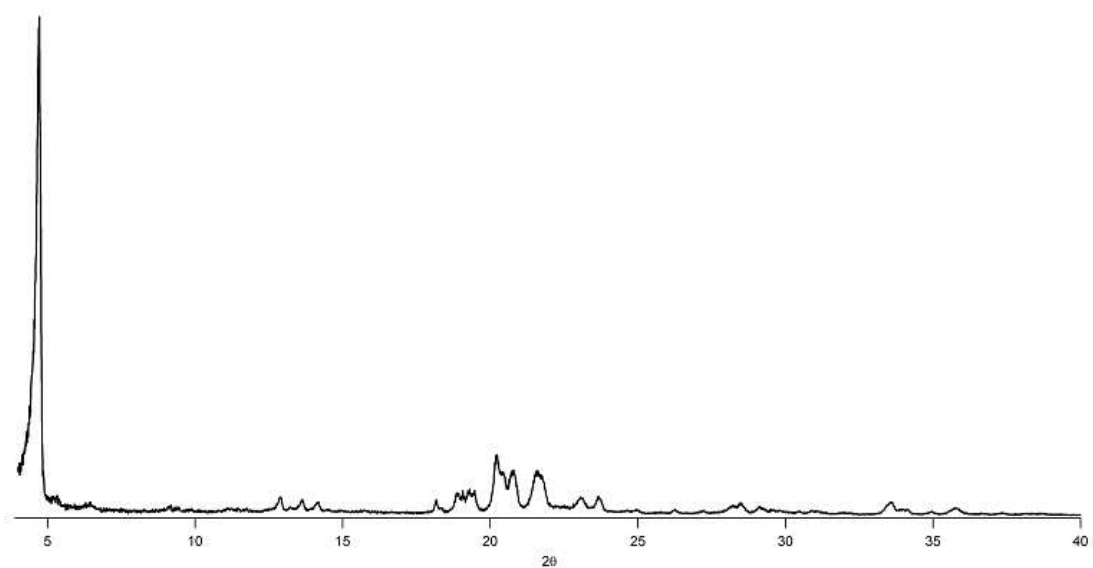
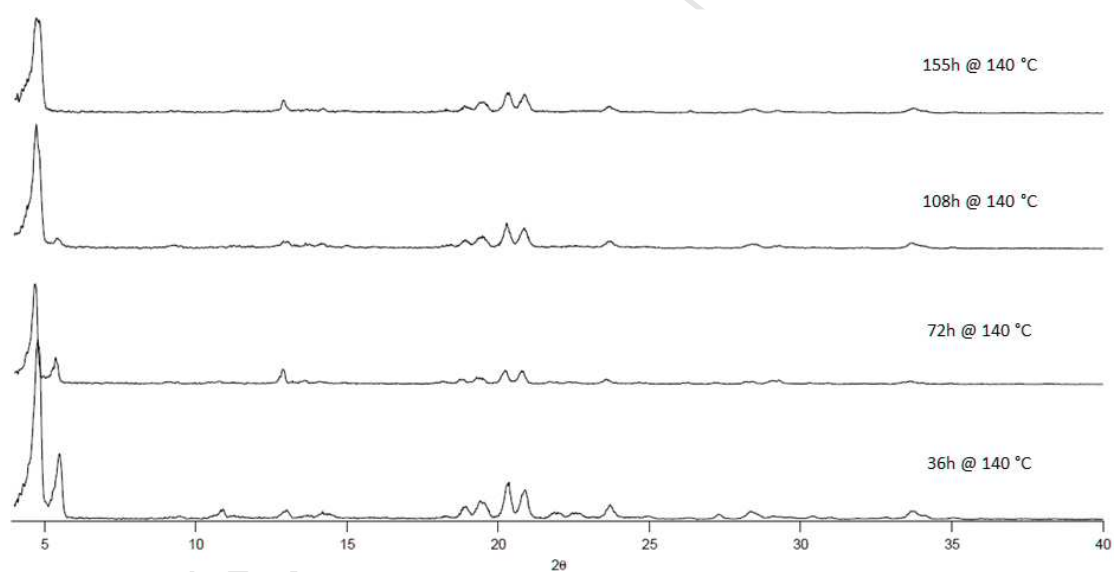


Figure 10

**Figure 11****Figure 12**

**Figure 13****Figure 14**

**Figure 15****Figure 16**

**Figure 17****Figure 18**

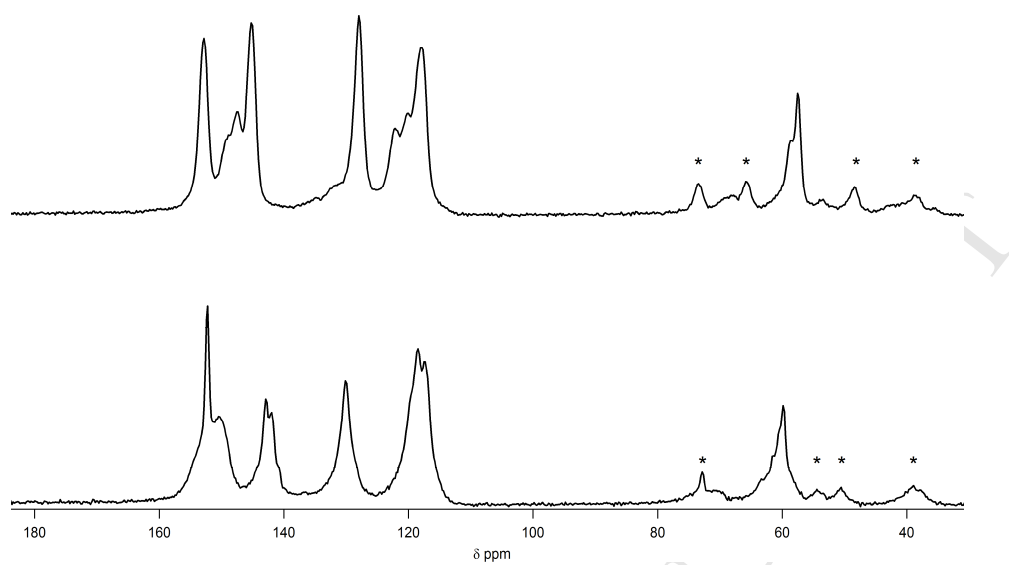


Figure 19

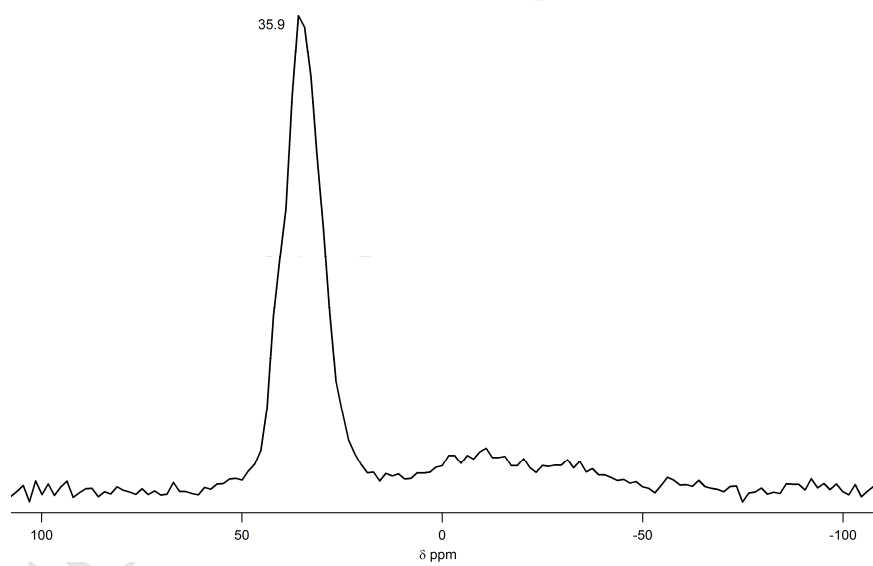
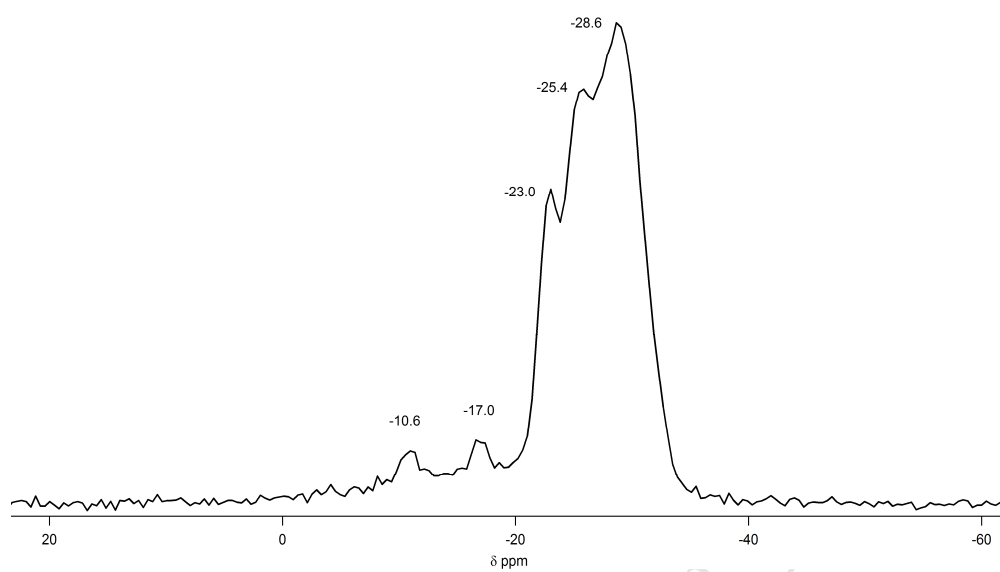


Figure 20

**Figure 21**

- Synthesis of triptycene-based OSDAs
- Extra-large pored aluminophosphate synthesis
- Synthesis of VPI-5